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## Hermetically Sealed 230°C MnO<sub>2</sub> Tantalum Capacitors

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### ABSTRACT

Certain electronic applications, such as oil and gas exploration drilling, are continuously demanding ever higher operating temperatures. Recently operating temperature requirements have increased from 200°C to 230°C with an increased operating life from hours to one thousand hours and beyond. This need is linked with the continuous development of oil drilling heads and sensors and their use for deeper drilling or drilling in more difficult geological conditions. Capacitors with high capacitance value are a common part of the electronic boards used in these applications, but over 125°C/175°C, available capacitor choice is very limited. Tantalum SMD capacitor technology has proved its reliability in operation up to 175°C and there is a limited choice of special designs up to 200°C. Long life wet tantalum capacitors up to 200°C are available from multiple sources, or up to 230°C with reduced operational life from a single source.

Hermetically sealed MnO<sub>2</sub> tantalum capacitors have demonstrated their ability to offer unique long life stability at 230°C combined with solid, stable and robust design. [1]. The next testing and development presented in this paper discusses the basic behavior of the solid hermetically sealed MnO<sub>2</sub> tantalum capacitor above 200°C. A certain type of "wear out" has been observed in a longer exposure at 230°C depending on applied voltage. Nevertheless, the basic capability of the capacitor meets the "best in class" requirement for 230°C 1000hours continuous operating life with 50% voltage derating. The paper discusses and summarizes the "wear out" phenomenon observed at temperatures above 200°C on these capacitors and impact of different voltage derating to operational life at 230°C.

## INTRODUCTION

Tantalum surface mounted capacitors with solid electrolyte have been the favored capacitor technology choice in many electronic devices for more than five decades, thanks to high stability, reliability and volumetric efficiency. The traditional cathode material -  $\text{MnO}_2$  - provides good mechanical robustness and relative temperature and humidity stability which suit many applications. The two major disadvantages of  $\text{MnO}_2$  tantalum capacitors are the thermal runaway failure mode and relatively high equivalent series resistance (ESR). Both of these disadvantages can be solved by using cathodes based on conductive polymers. Such parts provide lower ESR and safer failure mode, but conductive polymer strongly limits possible operating temperature [1]. Some application areas demand maximum temperatures exceeding  $125^\circ\text{C}$ . There are even more challenging demands for operating temperature in applications like oil drilling, where a further increase of operating temperature above  $200^\circ\text{C}$  is required. A solution to the problem of limited stability in erratic high temperature environments is use of a  $\text{MnO}_2$  cathode. But even  $\text{MnO}_2$  based cathode systems are subject to potential degradation if exposed to long durations of extreme conditions. Moulding epoxy resin degradation can also negatively influence capacitor performance during long-term storage at temperatures above  $125^\circ\text{C}$ , or even relatively short time exposure to very high temperatures exceeding the specification conditions [2]. Other changes can include oxidation, morphology changes or other mechanisms of degradation which all lead to reduction of the cathode conductivity resulting in increased ESR or reduction in capacitance. Keeping the capacitor's internal structure away from excessive humidity and oxygen can significantly increase its ability to withstand extreme temperatures. Both of these conditions can be maintained by using capacitors which are hermetically sealed with an inert or other atmosphere. Additionally, the relatively high ESR provided with a  $\text{MnO}_2$  cathode can be reduced by use of parallel connections of capacitors inside one package.

## HERMETIC SEALING

A new hermetically sealed SMD tantalum capacitor structure has been designed where the capacitor element is enclosed and hermetically sealed within a ceramic housing. Nitrogen as an inert gas is used in addition inside the hermetic package to inhibit thermal failure mode of the manganese dioxide solid electrolyte. Ceramic packaging has been selected for initial studies due to its solid mechanical robustness and its hermetic sealing capabilities. The capacitor element is attached to the ceramic housing by a common termination. The housing includes a lid that is placed on an upper surface of the ceramic side walls after the capacitor element is positioned within the ceramic housing. The lid is typically made of metal materials to achieve the appropriate hermetic performance. A resistance seam welding the lid process produces a weld and 100% testing of hermeticity is performed on all manufactured parts in order to verify and guarantee the hermeticity.

The ceramic housing and the capacitor element having similar shapes so that the capacitor element can be readily accommodated within the interior space to provide maximum volumetric efficiency.

## RESULT AND DISCUSSION

Stability studies of tantalum capacitors with high volumetric efficiency, hermetically sealed under an inert atmosphere in ceramic packages described in the above section have been performed. Both temperature and voltage derating combinations have been the subject of extensive studies. Results of standard  $\text{MnO}_2$  solid electrolyte cathode are presented as an example of the hermetic sealing effect in the section below.

Testing and analysis of tantalum surface mounted capacitors have been performed on  $100\mu\text{F}/35\text{V}$  capacitors with  $\text{MnO}_2$ . A tantalum anode having a length of 4.90 mm, a width of 4.80 mm, and a thickness of 2.60 mm was anodized at 125V in a liquid electrolyte to achieve the  $50\mu\text{F}$  target. A conductive coating was then formed by dipping the entire anode into an aqueous solution of manganese (II) nitrate and then decomposed at  $250^\circ\text{C}$ . A leadframe material was welded to an anode connective member and used to finish the capacitor elements. A cathode connective member was attached to the lower surface of the capacitor element using a silver adhesive. The cathode connective members were then glued to a gold

cathode termination and leadframe connective members were welded to a gold anode termination located inside a ceramic housing having a length of 12.50 mm, a width of 11.00 mm, and a thickness of 5.35 mm. Two anodes were assembled into one package in parallel connection. The resulting assembly was placed into a welding chamber and purged with inert nitrogen gas before seam welding between the seal ring and the metal lid and the seam welding process was performed. The hermeticity test was conducted using helium detector before and after the following individual test. Maximum helium leakage rate shall not exceed  $1 \times 10^{-8}$  atm cc/sec. of Helium. Such a specially designed ageing process was performed after the seam welding process.

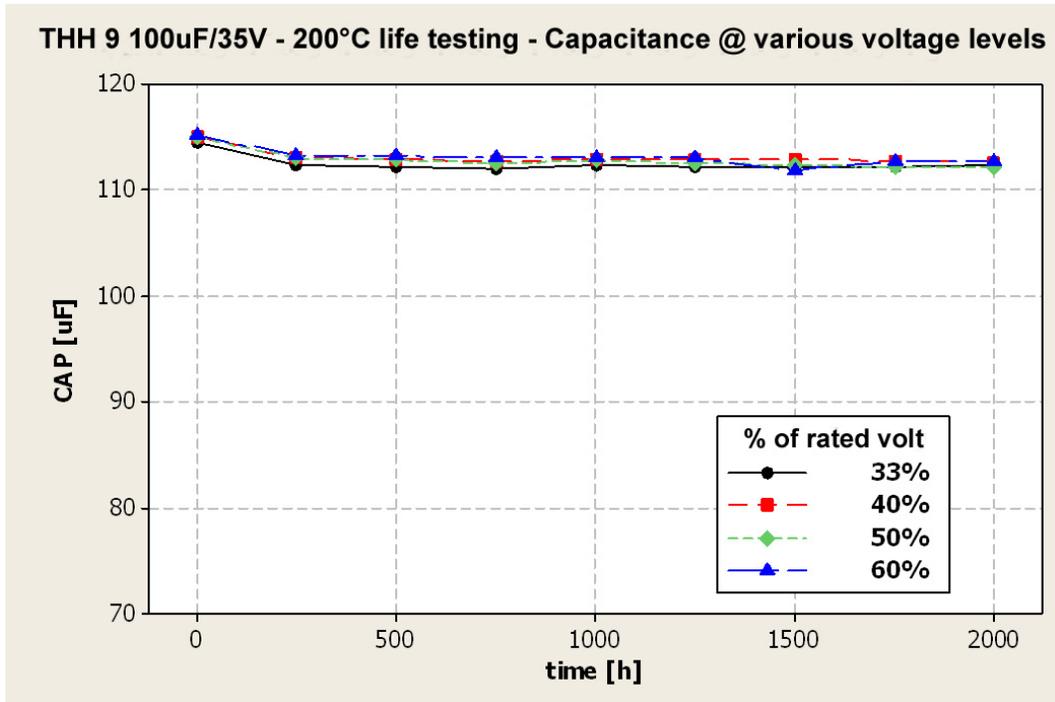
The test methods of electrical performance were applied at the following conditions: For life testing purposes, the capacitors were placed in an oven at the appropriate temperature with the desired voltage. A detailed description of all test methods is set out below.

- 1) Performance Life A: operating time 2.000hrs, test temperature 200°C, derating 0.33  $U_R$ , 0.40  $U_R$ , 0.50  $U_R$ , and 0.60  $U_R$
- 2) Performance Life B: operating time 1.000hrs, test temperature 230°C, 0V or derating 0.25  $U_R$ , 0.33  $U_R$ , 0.40  $U_R$ , and 0.50  $U_R$
- 3) Hot DCL after operating time @ Performance Life B: duration 60s, test temperature 230°C, 0.50  $U_R$
- 4) DCL after operating time @ Performance Life B: duration 60s, test temperature 20°C,  $U_R$

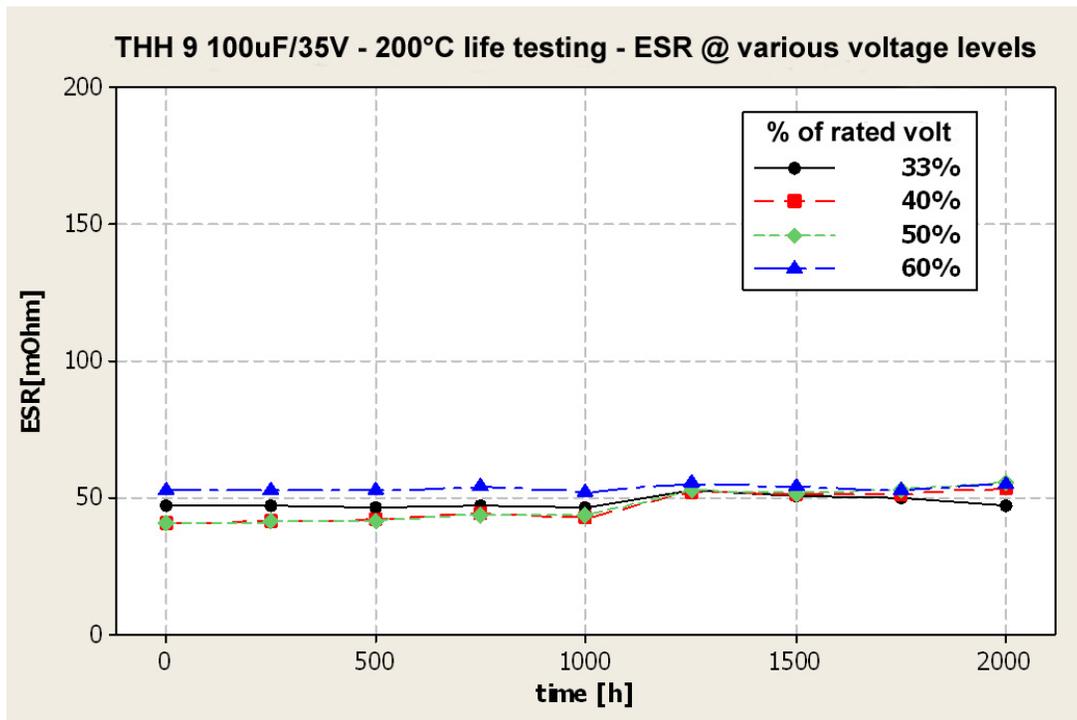
Capacitance was measured at 120Hz, 0.5RMS with DC BIAS of 2.2 volts. ESR was measured at 100 kHz. Leakage current at ambient temperature and at 230°C also was measured using a specially designed test set that measures leakage current at the rated voltage after a minimum of 60 seconds. All other measurements were performed at ambient temperature to verify whether the part exhibits any capacitance or ESR degradation. The results are set out below in Figures 1-6.

Figures 1 and 2 show changes in electrical results (capacitance and ESR) over time for parts tested at 200°C and different voltage rating levels 33 to 60%. No significant changes of capacitance and ESR were observed under these conditions within 2000 hours. Testing at 230°C and applied voltage 0 to 50% of rated voltage is plotted at Figures 3 and 4. No changes of capacitance are observed for measurement up to 33%  $V_r$  within 1000 hours. Slight capacitance reductions are observed for parts with 40-50%  $V_r$ , but the change is less than the tolerances allow. ESR at 230° is stable in the case of zero voltage was applied. For parts with an applied voltage, the ESR begins to increase after 500 hours and the rate of growth is proportional to the applied voltage. Thus in the worse case the ESR increased by 90% for 50%  $V_r$  at 230°C and 1000 hours. DCL for tests at 230°C and 50%  $V_r$  measured under hot (230°C) conditions (Figure 5) or at room temperature (Figure 6) showed a similar pattern – distribution of DCL is narrower and values drop after 500 hours of life, but then DCL values start to increase. A decrease of DCL during the first period of life can be explained by extended ageing of capacitors, the subsequent increase is due to structural changes of the dielectric under the test conditions.

Analyses of parts post test under 230°C and extended testing up to complete capacitance loss resulted in the cause of failure being identified.. The phenomenon of capacitance decrease is directly connected to conductivity changes in the cathode material –  $MnO_2$ . Figures 7 and 8 show FESEM photographs. Figure 7 shows high contrast with sharp edges, illustrating high conductivity of the  $MnO_2$  material. In Figure 8, after the life test the edges were observed to be blurred, evidencing lower conductivity of the  $MnO_2$  material. The mechanisms of conductivity degradation and morphological changes at temperature can be explained by chemical changes in the  $MnO_2$  cathode. The loss of oxygen could lead to formation of non-conductive oxides of Mn (like  $Mn_3O_4$ ). Thermal decomposition of  $MnO_2$  is well discussed in literature i.e. [3], but from tests of hermetically sealed capacitors it is obvious that voltage applied at elevated temperatures is the main factor driving decomposition.



**Figure 1: (Performance Life A) - results of capacitance during 2.000 hours @  $0.33 V_R$ ,  $0.40 V_R$ ,  $0.50 V_R$  and  $0.60 V_R$  of  $100\mu\text{F}/35\text{V}$  capacitors with cathode hermetically sealed in ceramic housing (median of 30 parts each)**



**Figure 2: (Performance Life A) - results of ESR during 2.000 hours @  $0.33 V_R$ ,  $0.40 V_R$ ,  $0.50 V_R$  and  $0.60 V_R$  of  $100\mu\text{F}/35\text{V}$  capacitors with cathode hermetically sealed in ceramic housing (median of 30 parts each)**

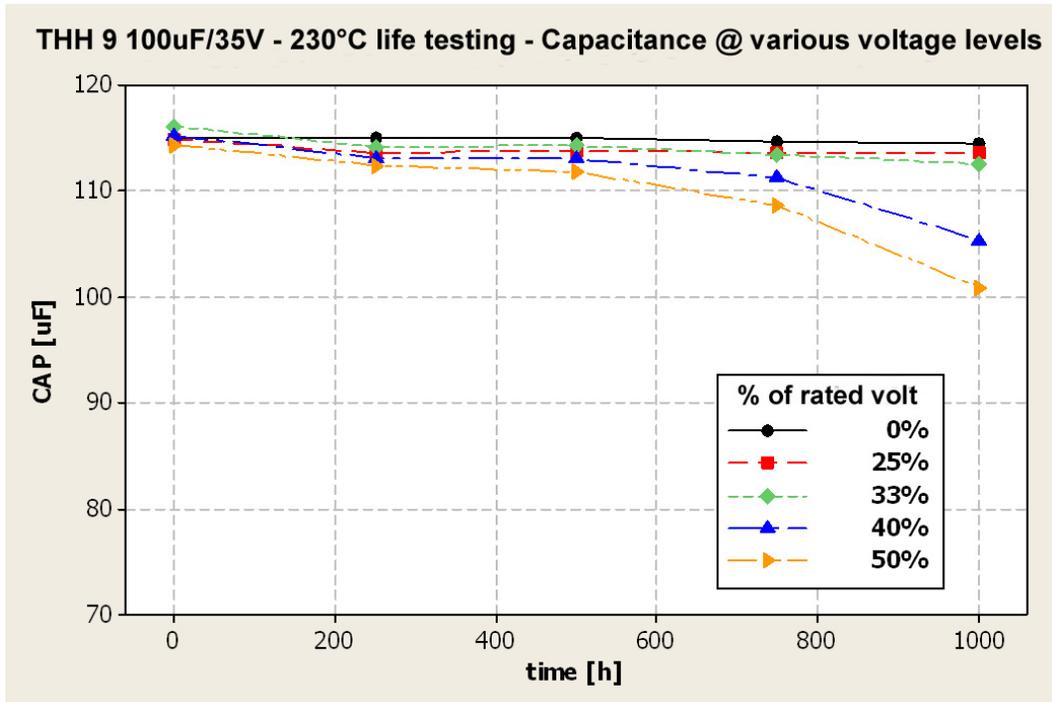


Figure 3: (Performance Life B) - results of ESR during 1.000 hours @ 0V, 0.25  $V_R$ , 0.33  $V_R$ , 0.40  $V_R$ , and 0.50  $V_R$  of 100 $\mu$ F/35V capacitors with cathode hermetically sealed in ceramic housing (median of 30 parts each)

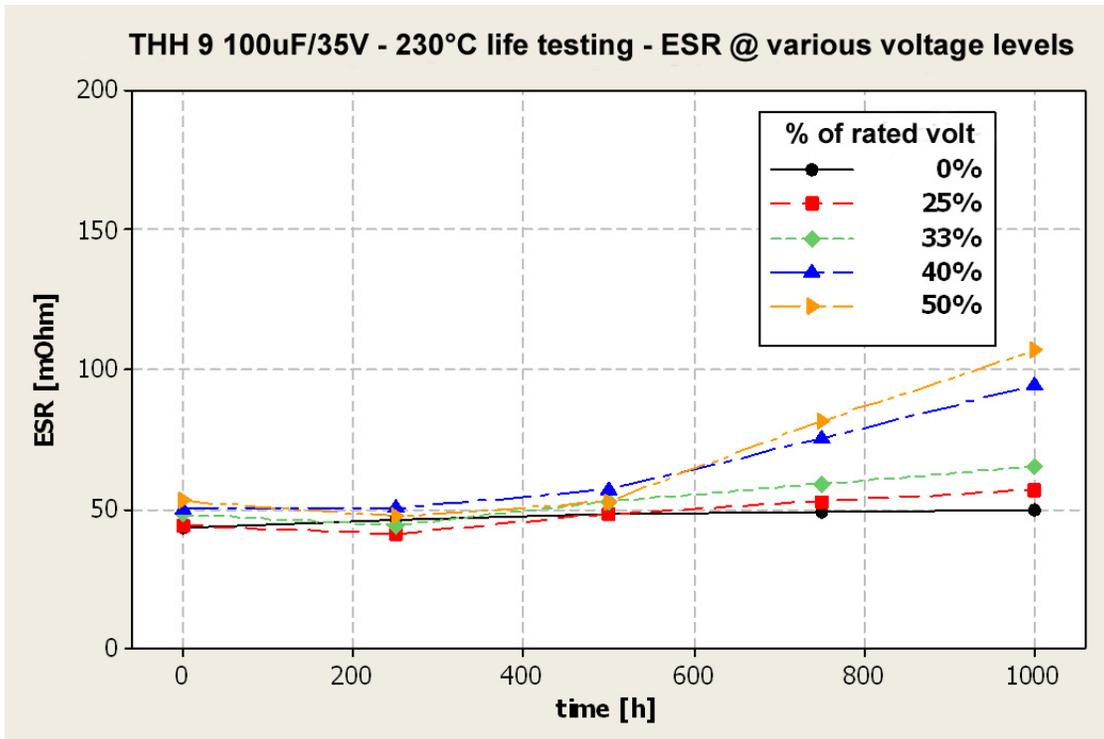
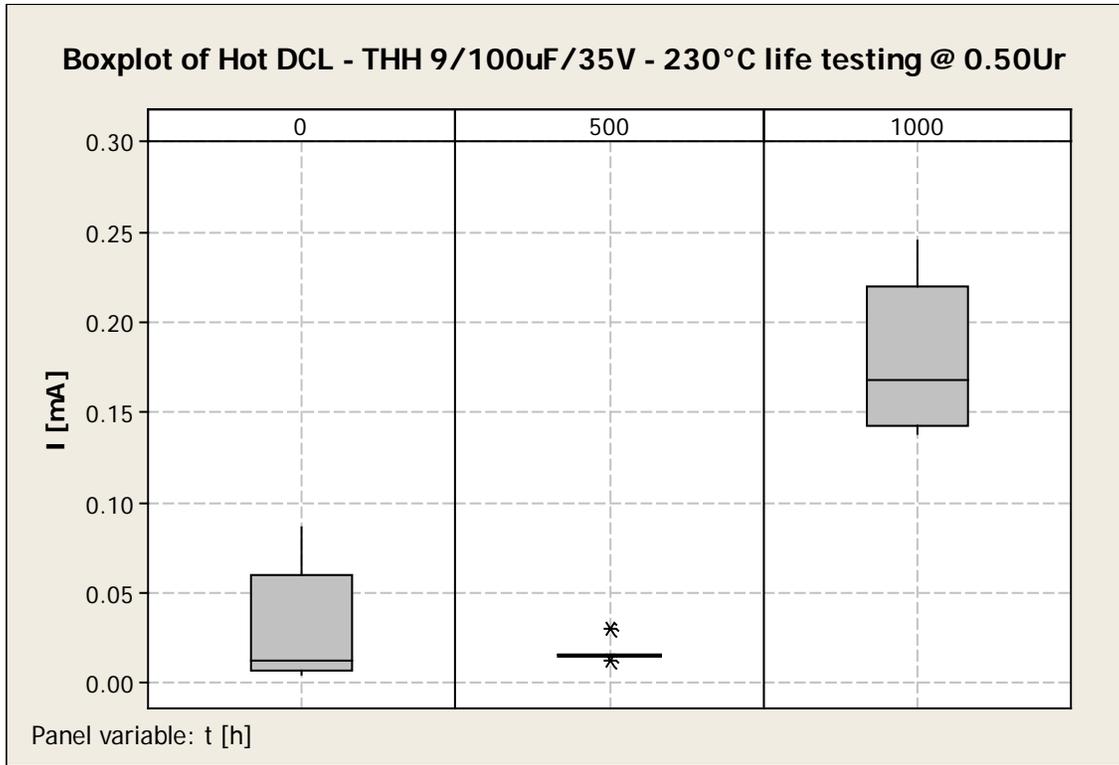
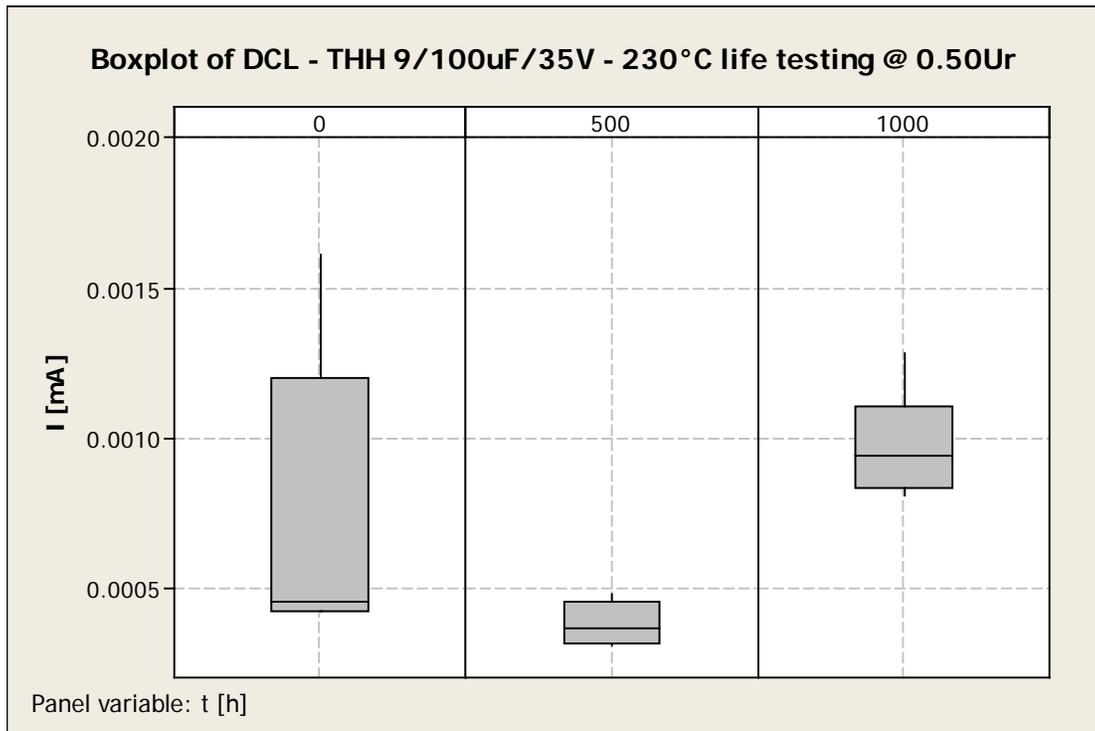


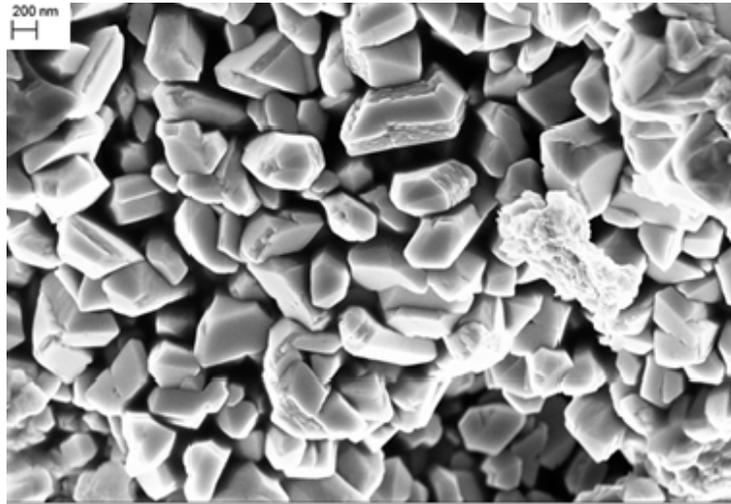
Figure 4: (Performance Life B) - results of ESR during 1.000 hours @ 0V, 0.25  $V_R$ , 0.33  $V_R$ , 0.40  $V_R$ , and 0.50  $V_R$  of 100 $\mu$ F/35V capacitors with cathode hermetically sealed in ceramic housing (median of 30 parts each)



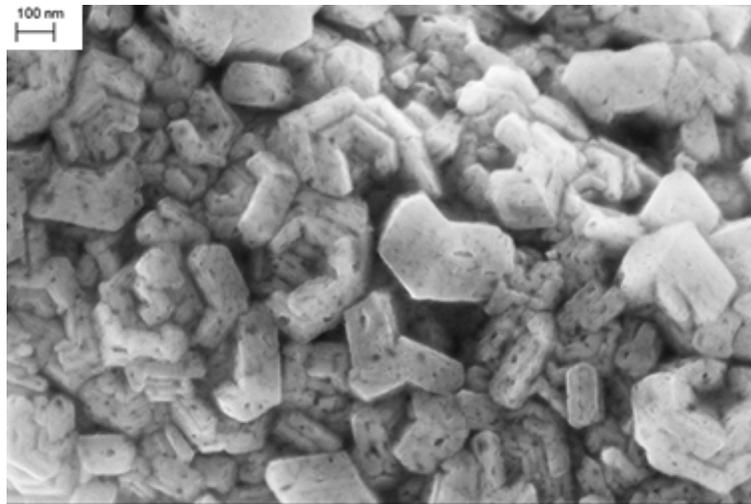
**Figure 5: (Performance Life B) - results of Hot DCL measured at 230°C during 1.000 hours @ 0.50  $V_R$  of 100 $\mu$ F/35V capacitors with cathode hermetically sealed in ceramic housing (boxplot of 30 parts)**



**Figure 6: (Performance Life B) - results of Hot DCL measured at ambient temperature during 1.000 hours @ 0.50  $V_R$  of 100 $\mu$ F/35V capacitors with cathode hermetically sealed in ceramic housing (boxplot of 30 parts)**



**Figure 7: results of FESEM analysis – MnO<sub>2</sub> cathode layer before Performance Life B of 100 $\mu$ F/35V capacitors with cathode hermetically sealed in ceramic housing)**



**Figure 8: results of FESEM analysis – MnO<sub>2</sub> cathode layer before Performance Life B (1.000 hours @ 0.50 V<sub>R</sub> of 100 $\mu$ F/35V capacitors with cathode hermetically sealed in ceramic housing)**

## CONCLUSIONS

Life tests performed on a new hermetically sealed SMD tantalum capacitor design show good stability at 200°C and voltage rating up to 60% of V<sub>r</sub>. Tests at 230°C show perfect stability in the case of zero voltage applied. Very good stability is obtained up to 33% of applied voltage; a further increment of voltage has an impact on ESR increase and slight capacitance decrease after 500 hours. DCL starts to grow after 500 hours in addition. A potential wear out mechanism was identified based on FESEM analysis as chemically and morphological changes of MnO<sub>2</sub> cathode induced by bias under elevated temperatures.

The observations shown in this paper are describing an as yet unpublished new wear-out mechanism for solid tantalum MnO<sub>2</sub> solid capacitors in application environments above 200°C that may limit operational life even in hermetically sealed packaging. Nevertheless, the key end users' requirement for continuous operational life time of 1000 hours at 230°C can be met with stable and reliable operation up to 50% of rated voltage (50% derating). As shown, 100 $\mu$ F/35V capacitors operating at 17.5V can provide good

stability up to 1000 hours at 230°C with final ESR below 100mOhms. This represents best in class performance of such high capacitance, small and stable SMD capacitor devices that may open up a new generation of designs for 230°C applications.

## REFERENCES

- [1] I. Zednickova, M. Biler, J. Petrzilek, T. Zednicek, Hermetically Sealed SMD Tantalum Capacitors, CARTS USA (2012).
- [2] T.Zednicek, J.Sikula, H.Leibovitz; A Study of Field Crystallization in Tantalum Capacitors and its effect on DCL and Reliability; CARTS USA (2009).
- [3] L. Li, M. He, A. Zhang, J. Zhou, A study on non-isothermal kinetics of the thermal decomposition of  $\beta$ -manganese dioxide, *Thermochimica Acta* 523 (2011)